Effects of pH, Electrolyte Concentration and Organic Acid Coating on the Aggregation Kinetics of Hematite Nanoparticles

Thesis

Presented in Partial Fulfillment of the Requirements for Honors Research Distinction

By

Pearl Chen

Undergraduate Program in Environmental Engineering

The Ohio State University

2018

Thesis Committee

Dr. John J. Lenhart, Advisor

Dr. Allison MacKay

Abstract

Natural aqueous systems contain dissolved organic matter as well as colloidal mineral particles, and the interactions between them in different environmental conditions are important because results have wide-spread application in water treatment and filtration. Hematite nanoparticles exhibit a high level of stability and predictability, making them an ideal model to study the effect of organic acids on mineral surface charges and the subsequent effect on the aggregation kinetics of environmentally ubiquitous nanoparticles. The organic acids that were studied are citric acid and humic acid, sourced from the Suwannee River. I explored the effects of varying electrolyte concentrations on the aggregation kinetics of the hematite particles, tested with either a citric acid or humic acid coating in solutions of environmentally relevant pH's.

The aggregation kinetics of bare hematite at pH's 4, 5, 6, 8, and 9 were measured. In each condition, the kinetics of bare hematite nanoparticles were measured by combining a hematite solution with varying concentrations of NaCl. After measuring the behavior of bare hematite nanoparticles, studies with ranging ionic strengths were conducted with a citric acid coating ranging from 100 μmol citric acid: 1 g hematite to 20,000 μmol citric acid: 1 g hematite. The effect of humic acid on hematite nanoparticles was conducted by using 0.5 mg/L humic acid to 100 mg/L hematite. Measurements were made using the Dynamic Light Scattering (DLS) apparatus, which measures the effective diameter of

solution particles as a function of time and indicates the aggregation of the solution over time. The data was analyzed to calculate the critical coagulation concentration (CCC). Major findings with this project had to do with the effect of changing pH, varying citric acid levels, and type of acid on the stability of hematite. It was found that at low pH, bare hematite was stable and stability decreased with a citric acid coating. At a high pH, bare hematite was unstable and stability increased with the addition of citric acid. In addition, it was found that at a high pH, larger acid concentrations led to greater stability. However, at a lower pH, the acid coating led to less stability. It was also found that a humic acid coating had a comparable effect on hematite stability as a citric acid coating when the humic acid had a 70x lower concentration.

This research has expanded on knowledge regarding hematite behavior in aqueous settings. Future work should be conducted on the effects of varying humic acid on the stability of hematite nanoparticles.

Dedication

Dedicated to my parents for their never-ending support.

Acknowledgments

I would like to thank all the faculty and staff of the Ohio State University who have contributed to my educational development during my time here. In particular, I would like to recognize Dr. John Lenhart for the opportunities and guidance he has offered me while being my research advisor. In addition, I would like to thank the College of Engineering for providing me with the chance to pursue this project.

Vita

May 2014……Olentangy Liberty High School

2014 to present…….....……B.S. Environmental Engineering, The Ohio State University

Fields of Study

Major Field: Environmental Engineering

Minor Field: Humanitarian Engineering

Table of Contents

List of Tables

List of Figures

1. Introduction

Iron oxide minerals are prevalent in environmental systems, and among them is hematite, which affects the distribution of natural organic matter in aqueous systems due to its interfacial processes. Solutions with hematite are unusually stable compared to most nanoparticle solutions, making hematite a suitable mineral to use as a model for how other mineral particles may behave in nature (Y. T. He, *et al*., 2007).

The aggregation rate of a particle solution is a measure of its stability, and a factor that influences the stability of a particle is its surface charge. Hydrated hematite nanoparticles exhibit an amphoteric nature, meaning that particle surfaces can react with both dissolved acids and bases, resulting in differing surface charges based on the pH of the particle solutions (E. Tombacz, 2005). As shown in Figure 1, at low pHs, minerals exhibit positive charges and at high pHs, minerals are negatively charged. This influences the solution stability since a high particle charge causes electrostatic repulsion, and therefore less coagulation.

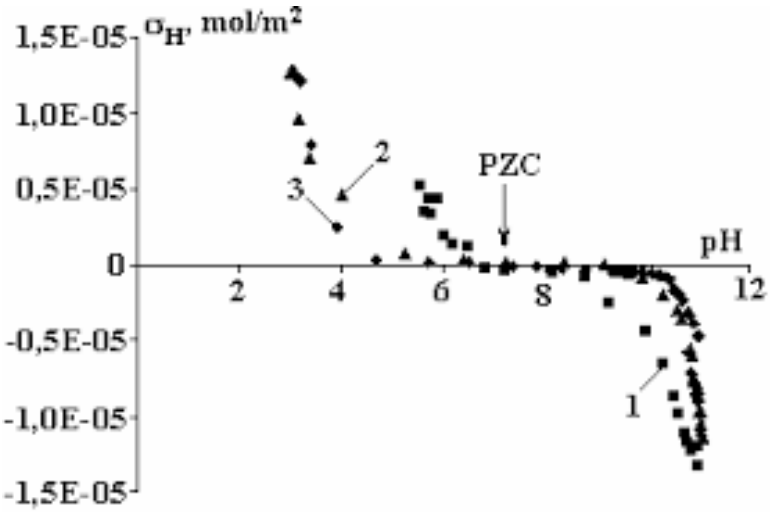

Figure 1: Zeta potential for hematite, PZC=7.8 (Phillipe et. al).

In a nanoparticle solution, the aggregation rate can be increased by adding salt, which compresses the electrical double layer of hematite particles and makes repulsive forces between them easier to overcome, increasing the aggregation rate because particles can then interact more readily. This electric double layer (EDL) is the net charge in the particle's surrounding interfacial region. When the electrostatic repulsive forces go down, the Van de Waals forces, or interparticle forces, go up, and the particles coagulate.

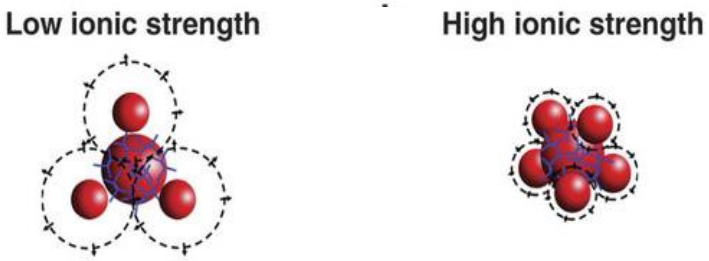

Figure 2. At high ionic strength, the EDL is suppressed (Chen et. al).

A way to assess a particle solution's stability is by measuring the CCC, or critical coagulation concentration. The critical coagulation concentration is the ionic strength at

which when particles collide, coagulation will always occur. It is a measure of a particle solution's stability since a higher CCC indicates that more salt is needed to induce aggregation. When at low salt concentrations, mineral particles repel from one another because they share the same surface charge. However, this electrostatic repulsion will be removed if the electric double layer on the nanoparticles are suppressed.

The charge of a particle solution, and subsequently the stability, is also a function of surface groups. The surface groups are affected by adsorption of naturally occurring acids such as citric and humic acids (Chen et. al). Citric acid is a homogeneous compound found naturally in soil, and it contains three carboxyl groups (R-COOH) and one hydroxyl group (R-OH).

Unlike citric acid, humic acid is a heterogeneous macromolecule that occur in natural environmental settings, meaning that it doesn't have any specific molecular identity. Since the functional groups between citric acid and humic acid are similar, lab results involving the two acids are comparable. A study conducted by Gu et al. determined that carboxyl and hydroxyl groups, both present in citric and humic acid, will interact directly with the surface of hematite. In addition, previous research has shown that very low amounts of citric acid can induce further aggregation, but a larger concentration of citric acid results in a more stable suspension of particles (E. Tombacz, 2005). Organic acids can alter the surface charge when adsorbed to mineral particles because unlike minerals, organic acids are negatively charged (Tiller et. al).

While research in hematite aggregation kinetics has been extensive, it is necessary to conduct testing of hematite behavior in systems with these naturally occurring acids.

Aside from the desire to remove mineral nanoparticles in aqueous systems, nanoparticles have also attracted interest in their application as a contaminant treatment technology (Y. T. He, *et al*., 2007). However, this application cannot be realized if the behavior in different environmental conditions is not understood, since the aggregation behavior impacts its reactivity and effectiveness in contaminant treatment. It is therefore crucial to gain a more thorough understanding of how nanoparticles behave in all environmentally relevant conditions.

The aim of my work was to discover the critical coagulation concentration (CCC) for hematite nanoparticles in systems with varying concentrations of citric and humic acids, both to obtain a wider dataset on nanoparticle behavior, and for the development of water treatment systems, high aggregation rates are desired since larger flocs of particles are easier to remove. When approaching this project, it was hypothesized that when coated with low amounts of acid, the solutions would become less stable (have lower CCCs), while more acid would lead to more stability (higher CCCs). In addition, at a pH lower than 7, it was suspected that the acid would absorb to the hematite and increase solution stability, while at elevated pH, less acid would adsorb and the solution would aggregate more quickly.

2. Methodology

2.1. Materials

The hematite particles used in this research were synthesized using the procedure described by Hwang et. al. with a size of 50 nm. Buffer solutions were created at pH 4, 5, 6, 8, and 9 using deionized water (Milli-Q, Millipore) and reagent grade $NaHCO_3$, NaOH, and HCl. Electrolyte solutions were prepared using reagent grade NaOH and using the buffer solution to keep them at the pH being tested for each experiment. All solutions were filtered through 0.2 μm cellulose ester membranes (Millipore) before use. Experiments were conducted using 4.5 mL cuvettes (BrandTech) and a Brookhaven Dynamic Light Scattering (DLS) instrument (90Plus, Brookhaven Instruments Corp., Holtsville, NY) device.

The DLS instrument works by measuring the effective diameter as a function of time. It does this by directing light through solutions and as the particles coagulated, the amount of light scattered would decrease, resulting in higher effective diameter over time. Tests were run until the diameter increased to 130% the original diameter. All aggregation experiments were conducted at a temperature of 22 ^{0}C.

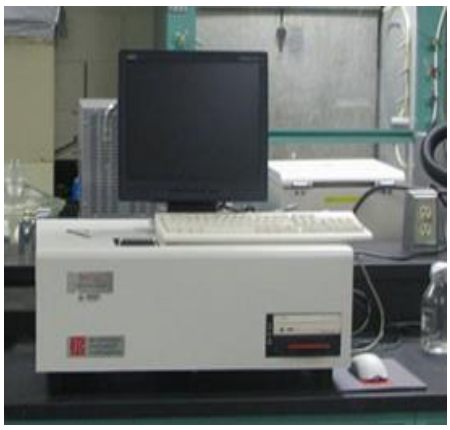

Figure 3. Brookhaven Dynamic Light Scattering apparatus.

2.2. Aggregation Kinetics

2.2.1. Bare Hematite

To conduct aggregation kinetics experiments of bare hematite at pH 4, stock hematite was diluted with pH 4 buffer to create a 240 mg/L hematite solution. After creating the pH 4 hematite solution, it, along with a pH 4 buffer solution, were both placed inside a sonicator bath for 5 minutes to disperse the particles. Immediately afterwards, a cuvette was filled with 250 μL of the hematite solution and 3.75 mL of the buffer solution (to get a hematite concentration of 15 mg/L). The cuvette was then quickly hand-shaken and placed in the DLS and the effective diameter was read using the particle sizing software. To achieve accurate results, it was crucial to place the cuvette in the DLS and start the software immediately after the solutions were combined in the cuvette. Experiments were then conducted with NaCl solutions at pH 4 ranging from 0.01-0.2 M NaCl, replacing the buffer solution in the cuvette. To ensure experiment precision, multiple trials were conducted for each scenario as well. Once all the concentrations of NaCl were tested, the

aggregation data were analyzed to calculate the CCC, as detailed in section 2.2.4. Similar tests with the bare hematite were conducted at pH 5, 6, 7, 8 and 9.

2.2.2. Hematite Coated with Citric Acid

Hematite coated with citric acid was created by using anhydrous citrate to create a solution that had 100 μmol citric acid per gram of hematite, with 240 mg/L hematite to stay constant with the bare hematite experiments. This was done by combining 240 mg of hematite with 24 μmol of citric acid (0.000504 g) in a 100 mL beaker, using pH 4 buffer as the solvent. This solution was filtered through a 0.45 um syringe-driven filter. A 0.2 M solution of NaCl was made at a pH of 4 and diluted to create solutions ranging from 0.001M to 0.2 M. All salt solutions were filtered with a 0.2 micron filter. Aggregation kinetics experiments were then conducted using 250 μL hematite and 3.75 mL citric acid-salt in a cuvette going into DLS. This process was repeated using citric acid -coated hematite solutions with 1000, 2000, and 20,000 μmol citric acid: 1 gram of hematite. In the cuvette, the concentration of hematite was always 15 mg/L, while the concentration of citric acid was 1.5 μM, 15 μM, 30 μM, and 300 μM for 100, 1000, 2000, and 20,000 μmol citric acid: 1 gram of hematite, respectively. The experiment was also repeated for pH 5, 6, 8, and 9; all the solutions detailed in this section were recreated at the pH being tested.

2.3.3. Hematite Coated with Humic Acid

100 mg/L humic acid stock acid was created by dissolving 25 mg of humic acid sourced from the Suwannee River (purchased from the International Humic Substances Society) in 250 mL DI water. The stock solution was stirred overnight on a magnetic stir plate, and filtered through a 0.45 um syringe-driven filter. This humic acid solution was then adjusted to pH 6 by using reagent grade HCl and NaOH, both filtered through a 0.2 micron filter.

A solution of 1 mg/L humic acid was then created at a pH of 6. Initial trials found that combining humic acid with hematite in one solution prior to entering the DLS, as with the citric acid experiments, resulted in the DLS being unable to produce rational results. Instead of combining the acid and hematite in one solution and mixing with a salt solution, separate hematite and humic acid solutions were created with salt concentrations of 0.01 – 2 M. Aggregation kinetics experiments were then conducted using 250 μL hematite and 3.75 mL humic acid-salt in a cuvette going into DLS. The concentration of hematite in the cuvette was 15 mg/L while the concentration of humic acid was 2.2 μM. This concentration was determined using 227.172 g/mol as the molecular weight.

2.3.4. Calculating the CCC

After kinetics experiments were conducted with different solution ionic strengths for each testing condition, an aggregation graph could be produced. A graph was considered sufficient if it appeared like Figure 4, where there is a wide variety of slopes shown, ranging from nearly flat, with low salt concentrations, to consistently high, as with the high salt concentration.

The slope of each line represents the rate of aggregation, and these slopes were used to calculate the α-value. The α-value is a proportion of the slope of a line to an average of the steepest slopes on the graph. The log of these α-values were plotted as a function of log of the ionic strength, which would produce a graph like Figure 4.

In Figure 4, it can be observed that there are two main trends: the steep line where the ionic strength has not reached the ones with the fastest slopes, and the flat line representing the fastest slopes. Two lines would be plotted to represent these trends and where the lines intersected would be used the log of the ionic strength at the CCC. Converting that value from a log to a number would give the CCC.

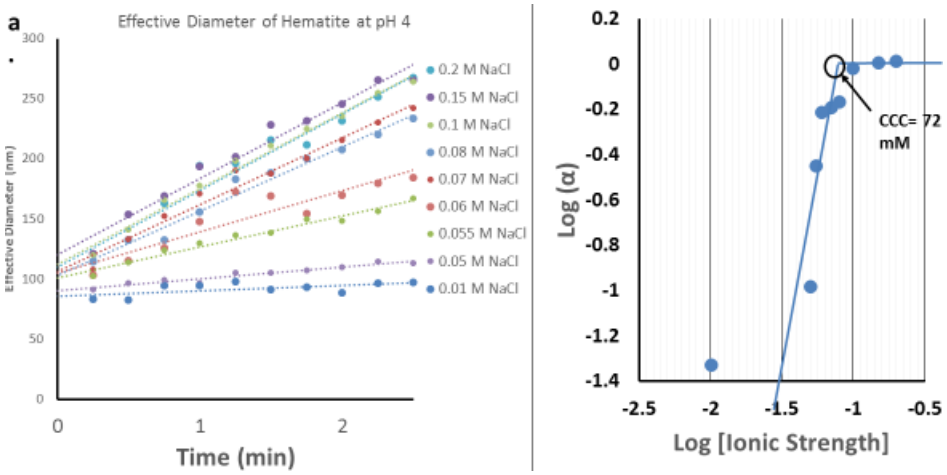

Figure 4. Aggregation results for bare hematite at pH 4.

3. Results

3.1. Bare Hematite Aggregation Kinetics

Aggregation kinetics experiments for hematite without acid showed that as pH increased, the particle stability decreased. This is seen in Figure 5 below. As pH moved from 4-6, there was a decrease in the CCC from 72, 63, and 32 mM; this means that as less salt was needed in solution to induce aggregation.

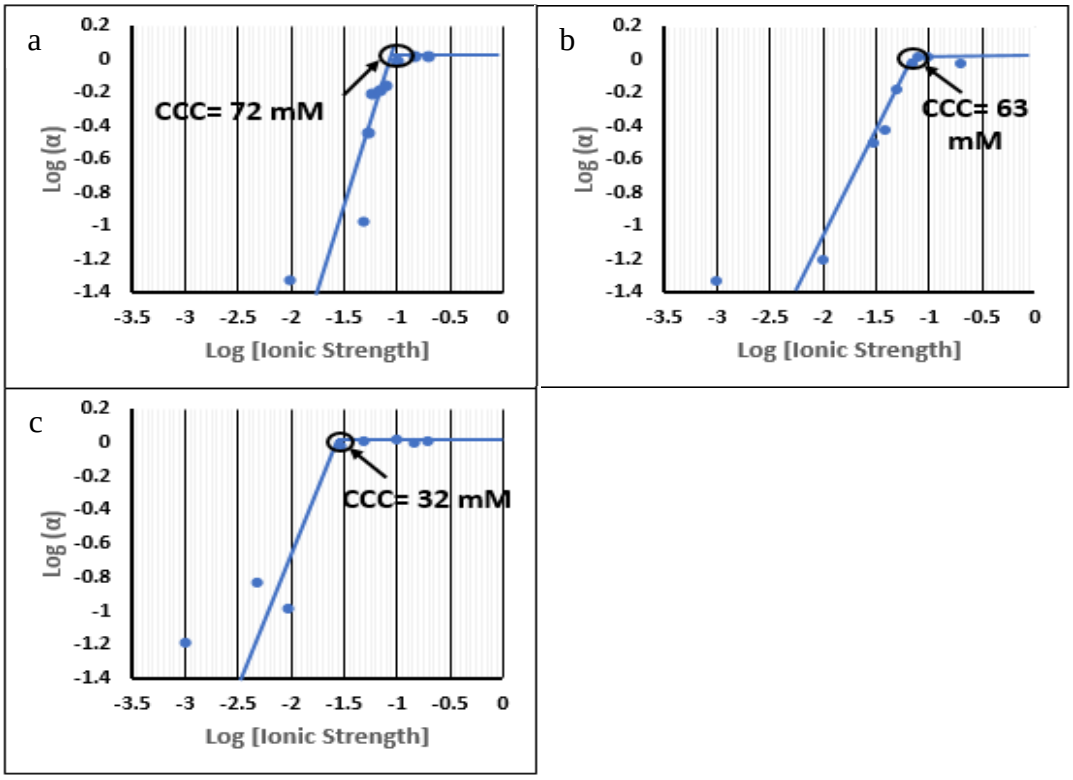

Figure 5: Aggregation results for pH (a) 4, (b) 5, (c) 6.

At the highest two pHs tested, 8 and 9, CCC graphs were not produced since they exhibited instant aggregation. As shown in Figure A1, the particles were measured as having an initial diameter of 500 nm at pH 9. This is impossible since the hematite particles were synthesized to be 50 nm, which was measurable for pH 4-6. Therefore, at pH 9, it can be assumed that the hematite particles instantly aggregated. Bare hematite at pH 8 was tested as well, but like at pH 9, there was instant aggregation and a CCC curve could not be produced.

3.2. Citric Acid Aggregation Kinetics

3.2.1. pH 4

It was observed that the addition of citric acid destabilized the hematite particles, but lower amounts of citric acid had a more drastic effect compared to higher amounts of citric acid. As seen in Figures A2 and A3, the lowest two concentrations of citric acid, 1.5 and 15 μM, lead to instant aggregation. This was gathered because it was not possible to get a flat curve at a low ionic strength.

Below, Figure 6 shows that at 30 μM citric acid and above, the solutions were stable enough for CCC graphs to be produced. Both 30 μM citric acid and 300 μM citric acid at pH 4 had low CCCs, 13 and 11 mM, which is much lower compared to that of bare hematite at pH 4, 72 mM.

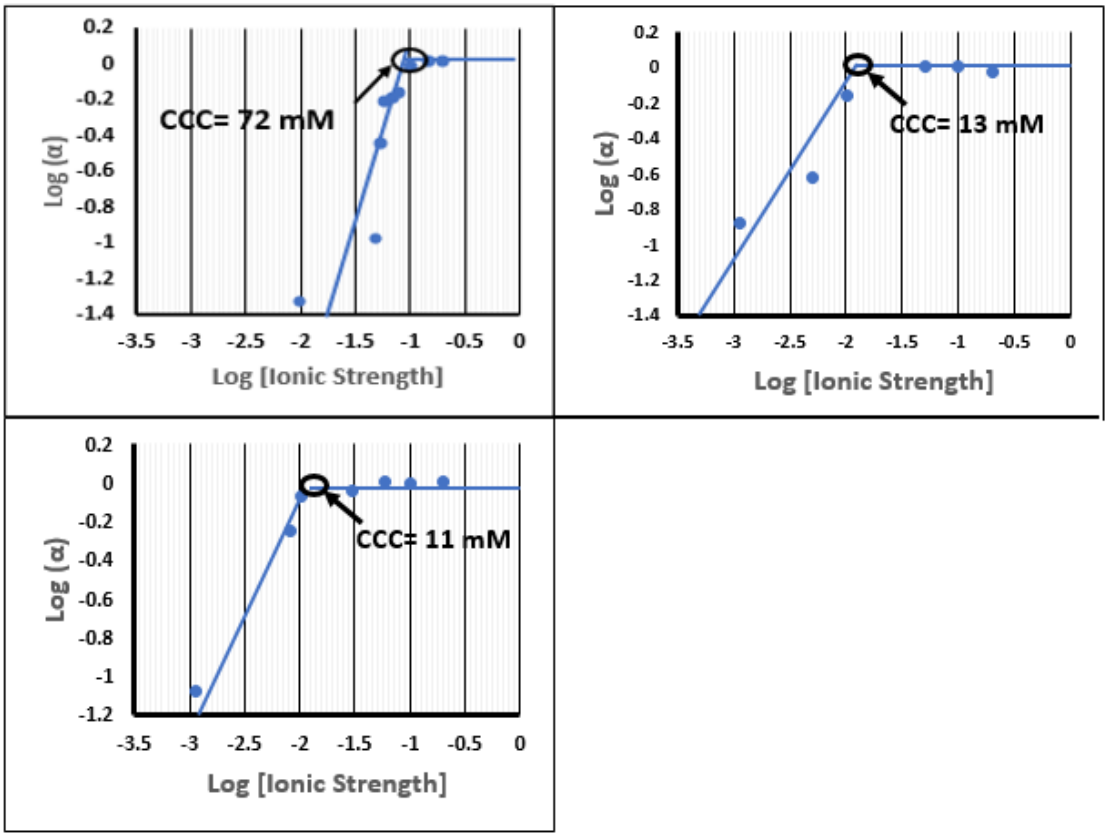

Figure 6: Results for (a) bare hematite (b) 30 µM citric acid (c) 300 µM citric acid, pH 4.

3.2.2. pH 5

Like at pH 4, experiments at pH 5 showed that the particle solution was initially stable, and small additions of citric acid lead to a major decrease in stability while large additions had a less obvious effect.

Figures 7 shows that a CCC was found for the 1.5 µM citric acid tested at pH 5. This value, 10 mM, was much lower than the CCC for bare hematite at pH 5, 63 mM. However, at 30 µM citric acid at pH 5, the CCC value was calculated to be 58 mM. Out of the citric acid concentrations tested, this was the most stable. It was comparable to the bare hematite at pH 5. This differed from what was observed at pH 4, where the lowest two concentrations of citric acid were instable, while the highest two concentrations were

more stable. In this scenario, the smallest concentration of citric acid tested had greater stability that the next highest and highest concentrations, but the second highest concentration had the smallest effect on the particle stability.

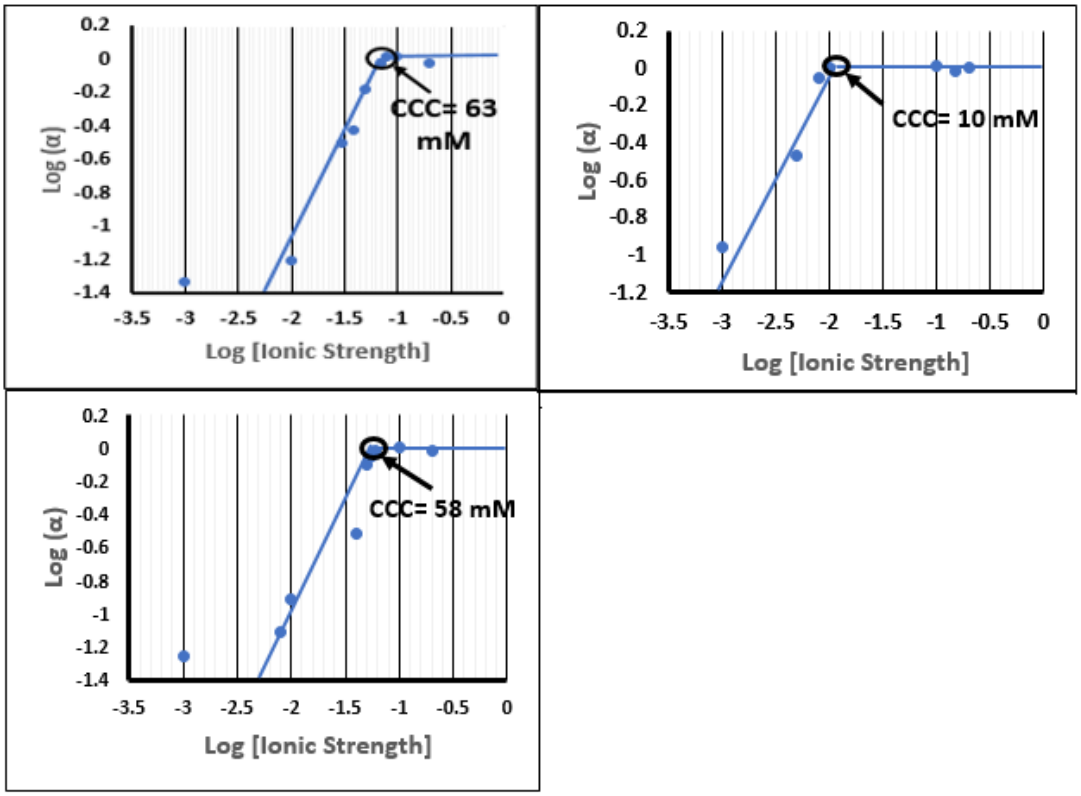

Figure 7: Results for (a) bare hematite (b) 1.5 uM citric acid (c) 30 uM citric acid at pH 5.

Figures A4 and A5 show that at 15 µM citric acid and 300 µM citric acid at pH 5 resulted in indiscernible effective diameter vs. time graphs, so CCCs could not be calculated for these conditions. At these concentrations of citric acid, particle aggregation was too rapid to be studied using the method described in this study.

3.2.3. pH 6

At pH 6, there was, again, a pattern of lower stability with the addition of acid. However, unlike at pH 4 and 5, all concentrations of citric acid below 300 µM lead to aggregation

graphs stable enough to calculate the CCC, as seen in Figures 14. At 1.5 µM citric acid, the CCC was low compared to that of the bare hematite, 32 mM. The same could be said for 15 µM citric acid, which had a CCC of 10 mM. However, at 30 µM citric acid, the solution was more stable than the bare hematite solution. The CCC was 79 mM, which was much higher than the CCC of bare hematite.

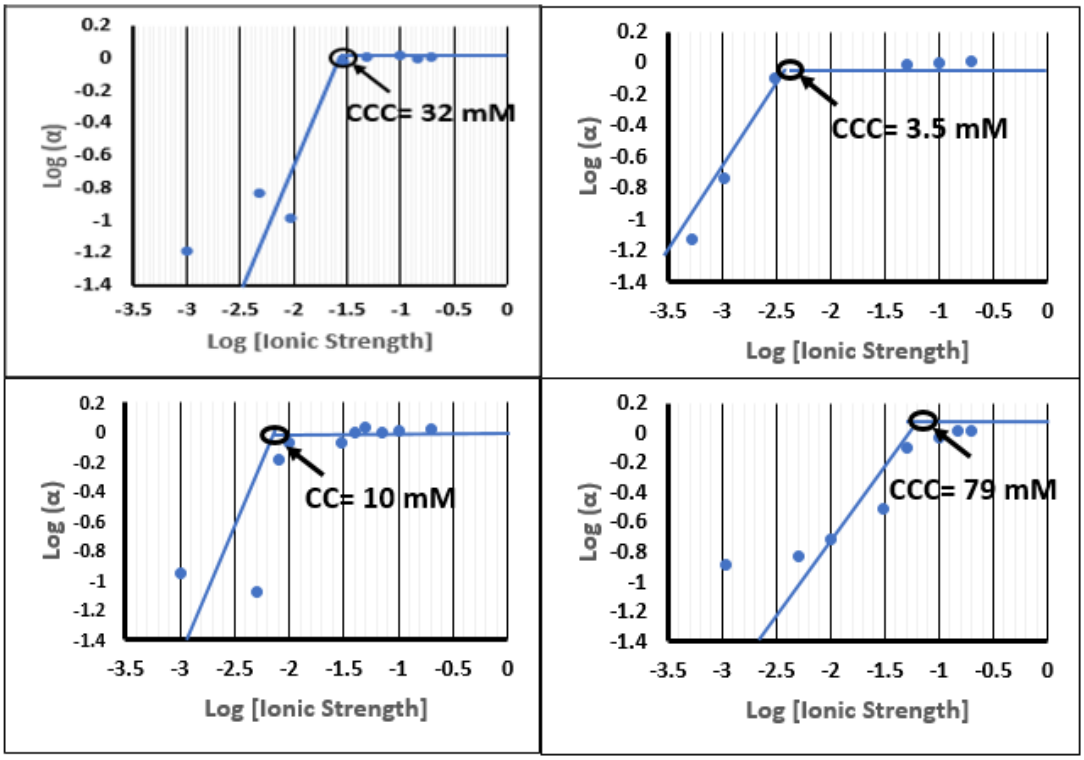

Figure 8: Aggregation results for (a) bare hematite (b) 1.5 µM citric acid (c) 15 µM citric acid (d) 30 µM citric acid at pH 6.

As shown in Figure A6, solutions that had an addition of 300 µM citric acid were not stable and aggregated instantly, so a CCC was not calculated for this condition.

3.2.4. pH 8

At pH 8, all solutions with citric acid tested exhibited greater stability than the bare hematite solution. pH 8 was the lowest pH tested in which citric acid increased the stability of hematite, rather than decreased. At this pH, it was impossible to measure a CCC for bare hematite since it aggregated instantly. However, as seen in Figure 9, at solutions higher than 1.5 µM citric acid, the stability increased, with the effect being more apparent at high acid concentrations. At 1.5 µM citric acid, the CCC was 19 mM, and at a higher acid concentration of 15 µM, the solution became even more stable with a CCC of 82 mM. Concentrations higher than 15 µM citric acid were not tested.

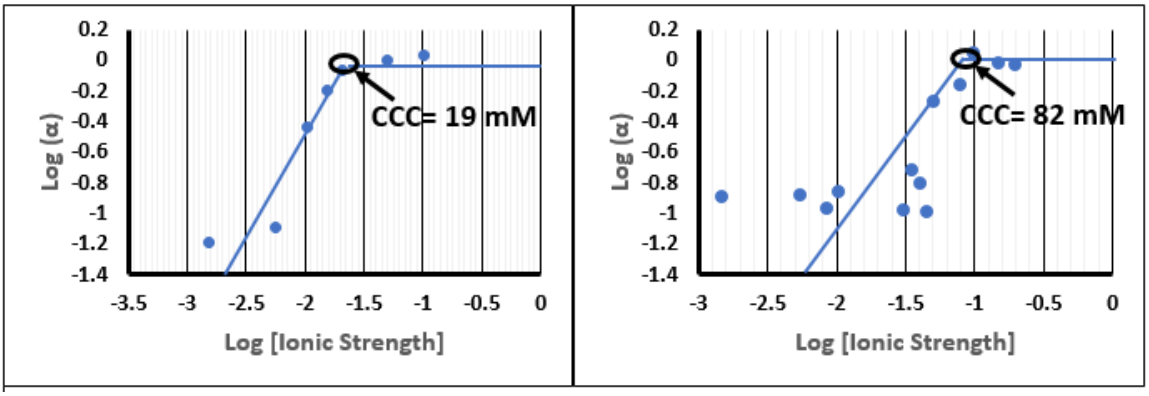

Figure 9: Aggregation results for (a) 1.5 µM citric acid (b) 15 µM citric acid at pH 8.

3.2.5. pH 9

Like at pH 8, bare hematite was unstable at pH 9 and aggregated instantly, while adding citric acid enhanced the stability. This added stability was more apparent at higher concentrations of citric acid. Adding 1.5 µM citric acid increased the CCC to 47 mM, as seen in Figure 10. At the highest citric acid concentration tested, 15 µM citric acid, the CCC was higher than that of 1.5 µM citric acid, 58 mM. Citric acid concentrations higher than 15 µM were not tested at this pH.

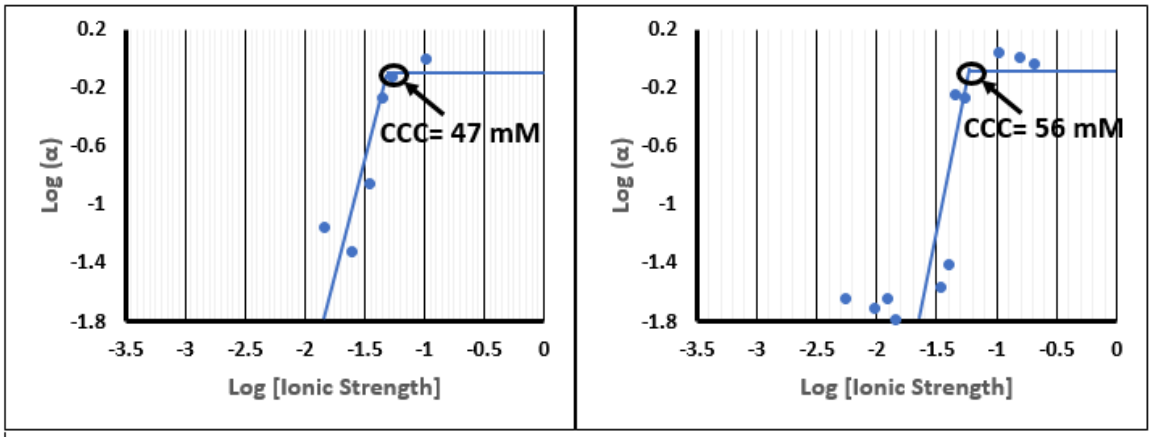

Figure 10. Aggregation results for (a) 1.5 μM citric acid (b) 15 μM citric acid at pH 9.

3.3. Humic Acid Aggregation Kinetics

Aggregation tests were conducted for hematite coated with Suwannee River humic acid. To determine the concentration of humic acid that would be tested, various concentrations of humic acid-coated hematite at pH 6 were run through the DLS to assess their stability. pH 6 was selected because at this pH, bare hematite is stable in solution, and pH 6 is environmentally relevant. As seen in Figure A7, 0.5 mg/L humic acid per 100 mg/L hematite as well as 3.0 mg/L humic acid per 100 mg/L hematite were both stable. 0.5 mg/L humic acid per 100 mg/L hematite, or 2.2 μM humic acid, was the condition used for the aggregation kinetics experiment. In this condition, the CCC calculated was 55 mM, as seen in Figure 11. This was higher than the CCC found for bare hematite at pH 6, 32 mM, which can be seen in Figure 8. The CCC for 2.2 μM humic acid was comparable to that of 30 uM citric acid.

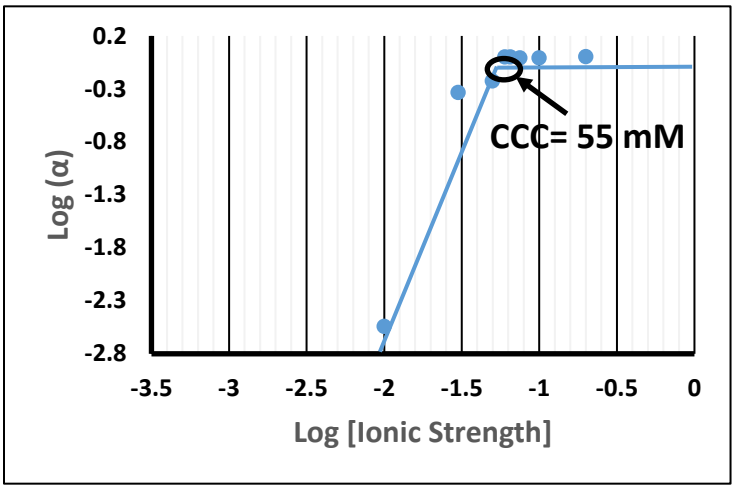

Figure 11. Aggregation results of 2.2 μM humic acid at pH 6.

4. Discussion

Table 1. Summary of CCCs found. All conditions were tested with 15 mg/L hematite. X represents conditions that were not tested.

Critical Coagulation Concentration (CCC) in mM					
	pH				
	4	5	6	8	9
Bare hematite	72	63	32	Unstable	Unstable
1.5 μM citric acid	X	10	3.5	19	47
15 μM citric acid	X	X	10	82	56
30 μM citric acid	13	58	79	X	X
300 μM citric acid	11	X	Unstable	X	X
2.2 μM humic acid	X	X	55	X	X

4.1. Effect of pH on stability of hematite

It was observed in the bare hematite experiments that as the pH increased from 4-9, the stability decreased. These results were consistent with hypothesis. From pH 4-6, bare hematite was stable, but the stability decreased as the pH got higher. At pH greater than 8, bare hematite was unstable. This trend corresponds to the zeta potential graph shown in Figure 1 for hematite measured by Phillipe et. al.

Hematite at pH 4-6 has a strong positive charge, which causes electrostatic repulsion to be the dominating force. As the charge gets closer to the x-axis, the CCC goes down, meaning that the repulsive forces are getting weaker. Once the zeta potential crosses the x-axis, the point of zero charge (PZC) is reached. The PZC describes when there is

negligible charge on the particle's surface, meaning that the repulsive forces are dominated by the van der Waals attractive forces (Mylon et. al). At this point, particles exhibit minimum stability, and therefore maximum coagulation, explaining why there is instant aggregation at the higher pHs tested, 8 and 9, since they are close to the PZC, 7.8. In addition, the charge of bare hematite went from positive to negative as the pH was raised. At low pH, hematite particles are prevented from coagulating due to high repulsion of the positively charged surfaces (Liang et. al). He et. al. also found that bare hematite nanoparticles started to aggregate when pH was greater than 8. This is because as the pH increases, functional groups on the surface deprotonate. This reduces the positive charge of hematite, leading to rapid aggregation of the particles.

4.2. Effect of Citric Acid Acid Concentration on Hematite Stability

It was found that at a high pH, larger acid concentrations led to greater stability. However, at a lower pH, the acid coating led to less stability. These results differed from the hypothesis regarding the effect of acid concentration on stability. Phillipe et al. describes that when the surface of a mineral is positively charged, the negative charge of the organic acids will cancel out the positive charge on the surface of the molecule, leaving the charge neutral. Without the strong surface charge, the particles will not have electrostatic repulsion preventing aggregation, which could be why at low pH, the addition of acid destabilizes the hematite solution. The opposite is true for solutions of pH greater than 8. The negative acid coating the negative surface charge of the hematite

particles could increase the magnitude of negative charge, which electrostatically stabilizes the particle solution.

At low pH, it was found that smaller acid concentrations had a greater effect on destabilizing the hematite particles. This could be because small amounts of acid would neutralize the positive surface charge of the hematite, reducing the Coulomb forces repelling the particles. At higher acid concentrations, hematite at pH 4 became more stable, which could be due to a reversal of the surface charge from positive to negative. Adding a large enough amount of acid would alter the net surface charge of the hematite nanoparticles (Tiller et. al).

4.3. Differences Between Citric Acid and Humic Acid

Table 2: Effects of humic acid and citric acid on hematite stability at pH 6.

	Bare hematite	1.5 uM citric acid	15 uM citric acid	30 uM citric acid	300 uM citric acid	2.2 uM humic acid
CCC in mM NaCl	32	3.5	10	79	Unstable	55

The effect of humic acid on hematite stability was found to be much stronger compared to the effect of citric acid. Table 2 shows that unlike most of the pH 6 acid conditions, humic acid had a positive effect on the stability of the solution. This was observed with 2.2 μM humic acid, but only with 30 μM citric acid. It was interpolated that the humic acid condition performed similarly to that of citric acid at a 70 times greater concentration. The reason for this could be that the molecule of humic acid is much

larger, so the layer of negative charge forms much more readily around hematite compared to the citric acid. According to Tombácz et. al, the adsorption of humic acid on minerals leads to an enhanced electrostatic stabilization of particles. Even at pHs where the zeta potential of bare hematite is positive, such as pH 6, the humic acid layer causes the particles to have a strong negative charge, preventing aggregation due to electrostatic repulsion. Gu et. al found that large molecules are adsorbed preferentially compared to smaller molecules, so since humic acid is much larger, the layer of negative charge around the particles forms more readily and provides greater stability than with citric acid. In addition, Mylon et. al found that humic acid will lay flat on the surface of mineral colloids rather than extend linearly from the surface. This would limit the electrosteric interactions between the hematite nanoparticles.

5. Conclusion

Hematite nanoparticles are environmentally ubiquitous, and to understand their behavior in natural systems, it is crucial to not only study the behavior of the particles on their own, but also to study the behavior when interacting with other components of that system. To observe how environmental changes affected the stability, factors such as the type and concentration of organic acids, as well as system pH, were manipulated. Aggregation kinetics experiments were conducted with bare hematite at pHs 4, 5, 6, 8, and 9. These experiments were then replicated with citric acid coating the hematite at concentrations ranging from 1.5 to 300 μM citric acid. The effect of humic acid on hematite nanoparticles was observed by using a concentration of 2.2 μM humic acid to 15 mg/L hematite.

The critical coagulation concentration (CCC) was calculated for each testing condition and used as a measure of the particle stability. It was found that the results for bare hematite were consistent with the hypothesis. In addition, the varying acid levels did not have a consistent effect on the stability, but rather, it depended on the system pH. In addition, humic acid had a greater ability to stabilize hematite than citric acid in the conditions tested. Future work in this subject should be done to expand the dataset of humic acid's effect on hematite nanoparticle stability, but this project was able to increase the knowledge on hematite's behavior in various conditions.

Bibliography

Chen, KL, SE Mylon, and M Elimelech. "Aggregation Kinetics of Alginate-Coated Hematite Nanoparticles in Monovalent and Divalent Electrolytes." *Environmental Science & Technology*. 40.5 (2006): 1516-23. Print.

Chen, KL, SE Mylon, and M Elimelech. "Enhanced Aggregation of Alginate-Coated Iron Oxide (Hematite) Nanoparticles in the Presence of Calcium, Strontium, and Barium Cations." *Langmuir*. 23: (2007): 5920-5928. Web. 8 Feb 2017.

He, Y T, Jiamin Wan, and Tetsu Tokunaga. "Kinetic Stability of Hematite Nanoparticles: the Effect of Particle Sizes." *Journal of Nanoparticle Research : an Interdisciplinary Forum for Nanoscale Science and Technology*. 10.2 (2008): 321-332. Print. 8 Feb 2017.

Hwang, Yu S, Jin Liu, John J. Lenhart, and Christopher M. Hadad. "Surface Complexes of Phthalic Acid at the Hematite/water Interface." *Journal of Colloid and Interface Science*. 307.1 (2007): 124-134. Print. 8 Feb 2017.

Mylon, SE, KL Chen, and M Elimelech. "Influence of Natural Organic Matter and Ionic Composition on the Kinetics and Structure of Hematite Colloid Aggregation: Implications to Iron Depletion in Estuaries." *Langmuir : the Acs Journal of Surfaces and Colloids*. 20.21 (2004): 9000-6. Print. 8 Feb 2017.

Philippe, Allan and Schaumann, Gabriele E. "Interactions of Dissolved Organic Matter with Natural and Engineered Inorganic Colloids: A Review." *Environmental Science & Technology*. 10.1021 (2014): 8946-8962. Print. 1 November 2018.

Tiller, Christine and O'Melia, Charles. "Natural organic matter and colloidal stability: Models and measurements." *Colloids and Surfaces A: Physicochemical and Engineering Aspects.* 89-102 (1993): 10.1016/0927-7757(93)80009-4. Print. 1 November 2018.

Tombacz, E. "The Effect of Humic Acid Adsorption on Ph-Dependent Surface Charging and Aggregation of Magnetite Nanoparticles." *Journal of Colloid and Interface Science*. 295.1 (2006): 115-123. Print. 8 Feb 2017.

Appendix A. Raw Aggregation Kinetics Data

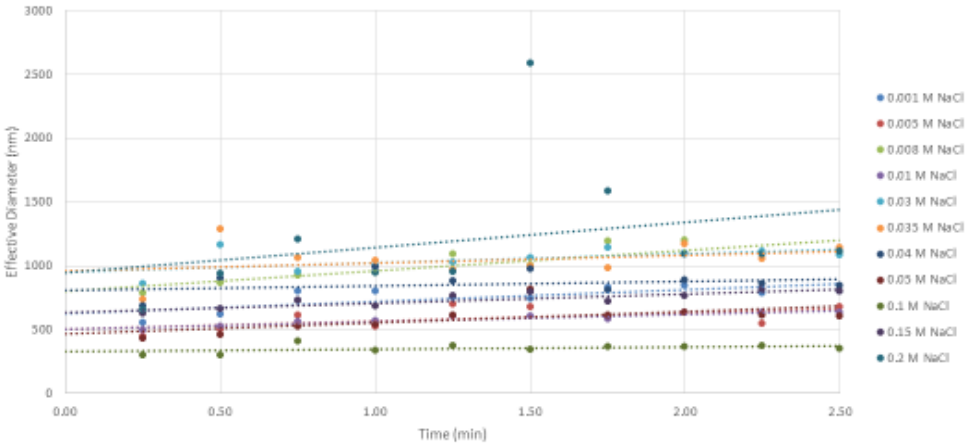

Figure A1. Aggregation results of hematite at pH 9.

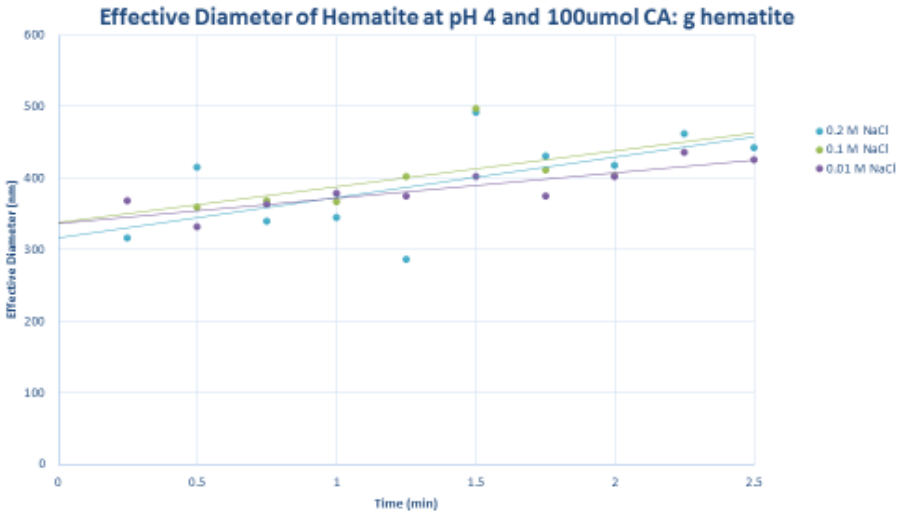

Figure A2. Aggregation results of 1.5 uM citric acid at pH 4.

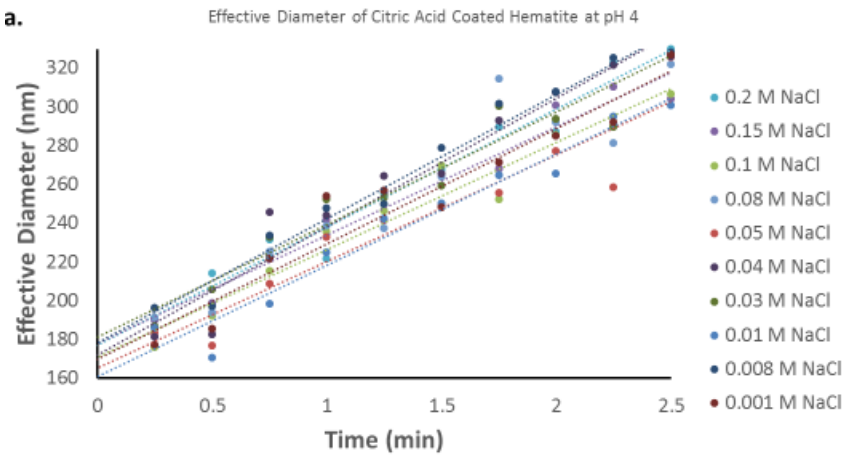

Figure A3. Aggregation results of 15 uM citric acid at pH 4.

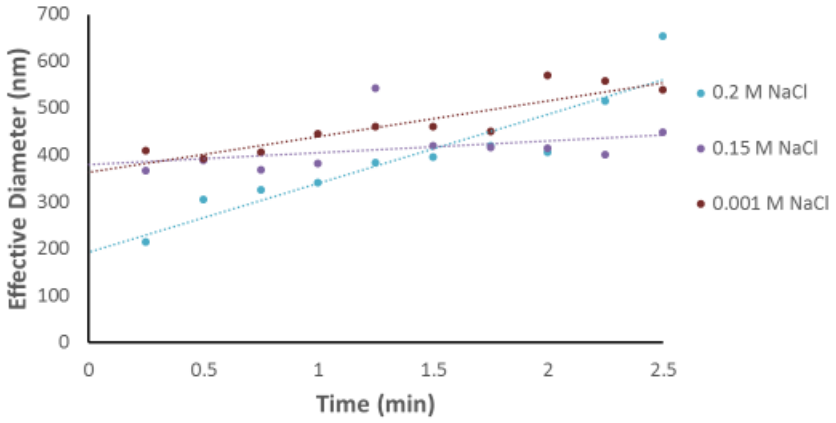

Figure A4. Aggregation results of 15 uM citric acid at pH 5.

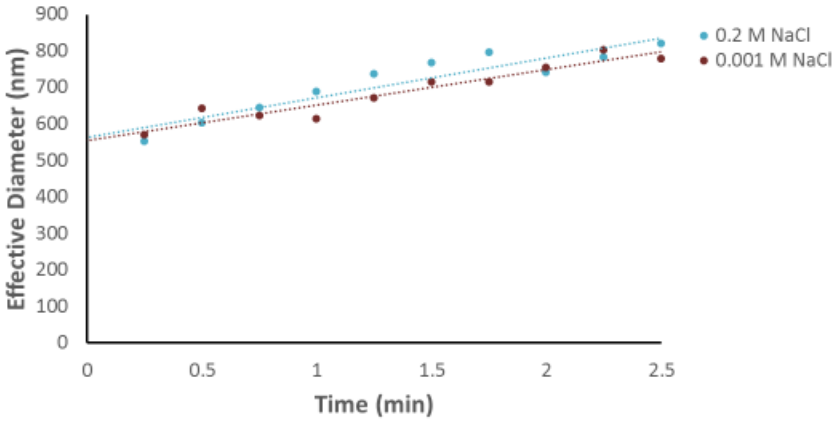

Figure A5. Aggregation results of 300 uM citric acid at pH 5.

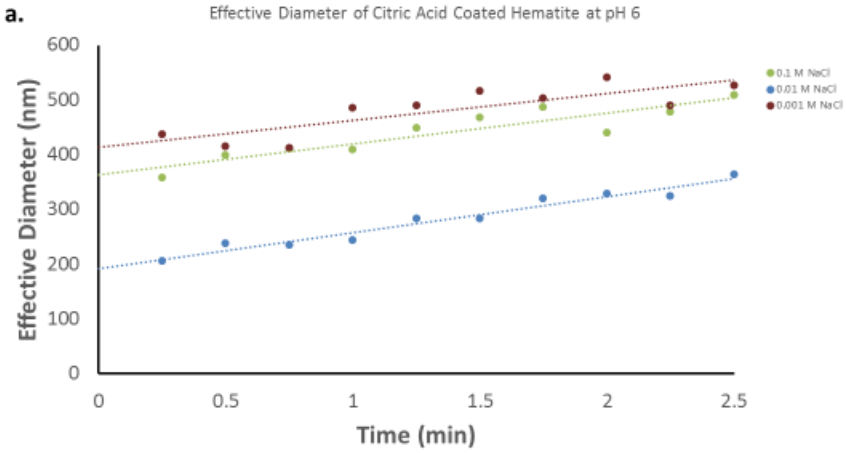

Figure A6. Aggregation results of 15 uM CA at pH 6.

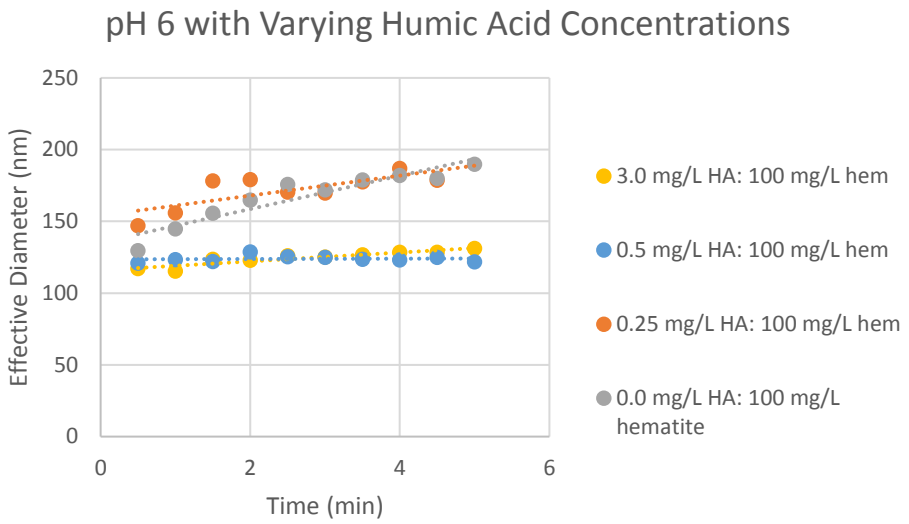

Figure A7. Humic acid concentrations at pH 6

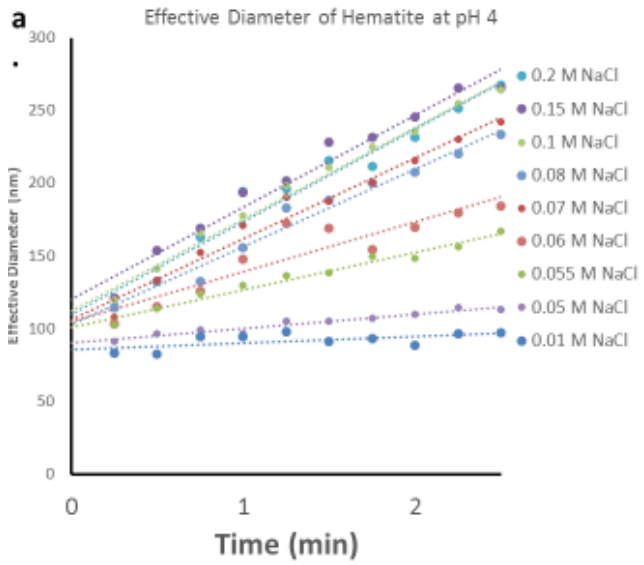

Figure A8. Aggregation results for bare hematite at pH 4.

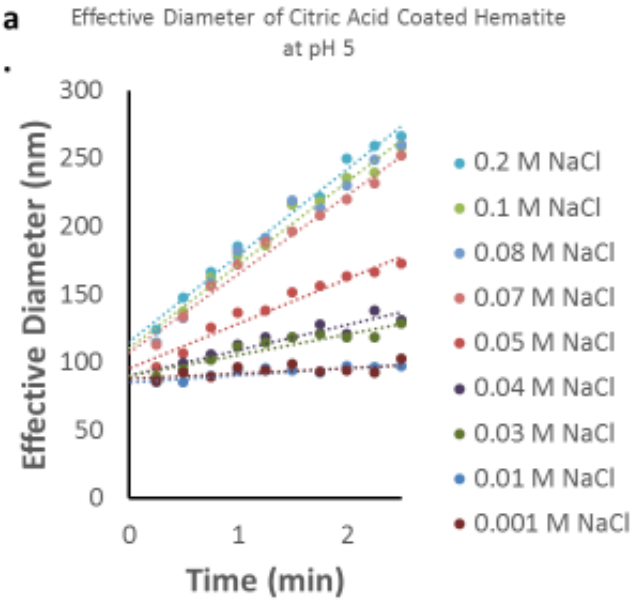

Figure A9. Aggregation results of hematite at pH 5.

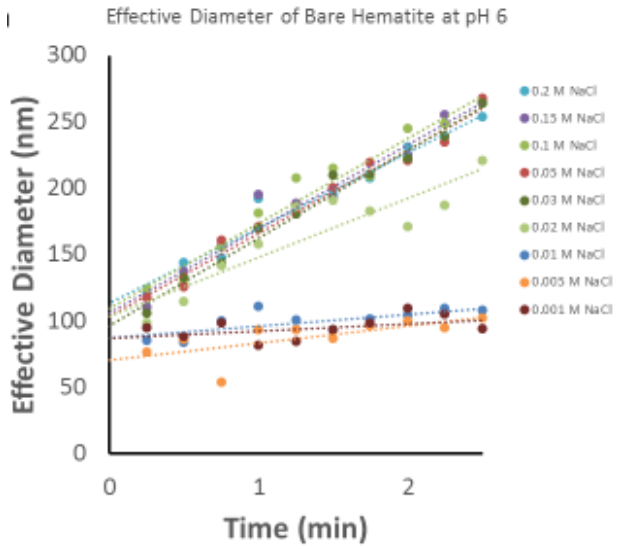

Figure A10. Aggregation results of hematite at pH 6.

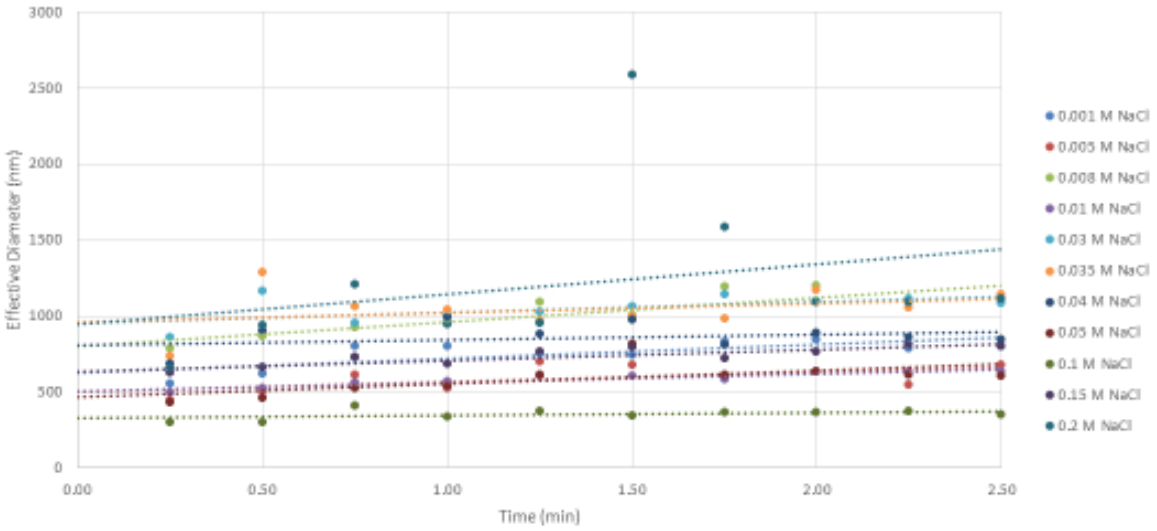

Figure A11. Aggregation results of hematite at pH 9.

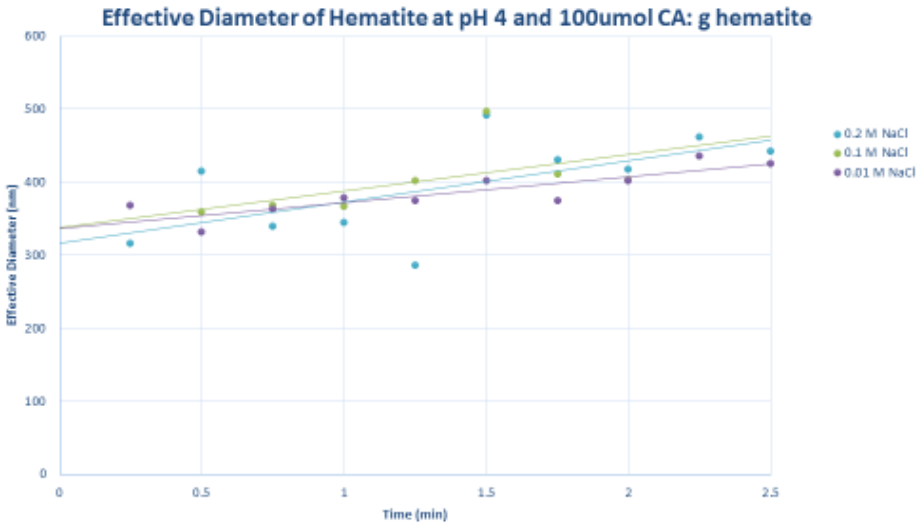

Figure A12. Aggregation results of hematite with 1.5 µM citric acid at pH 4.

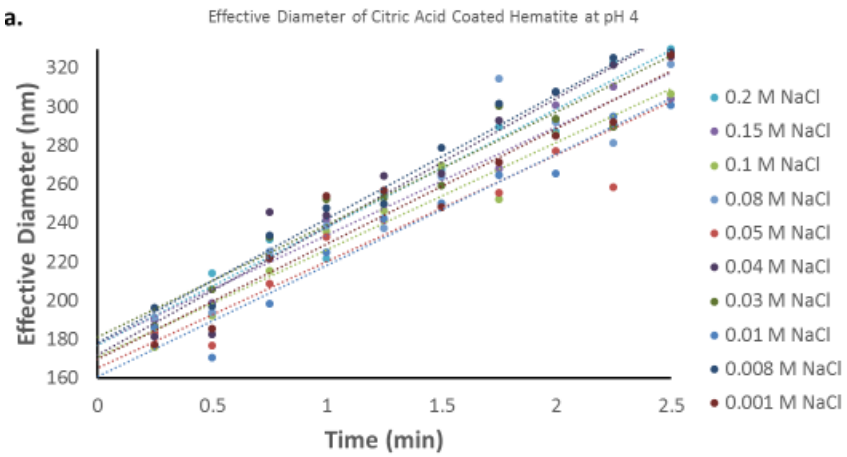

Figure A13. Aggregation results of hematite with 15 µM citric acid at pH 4.

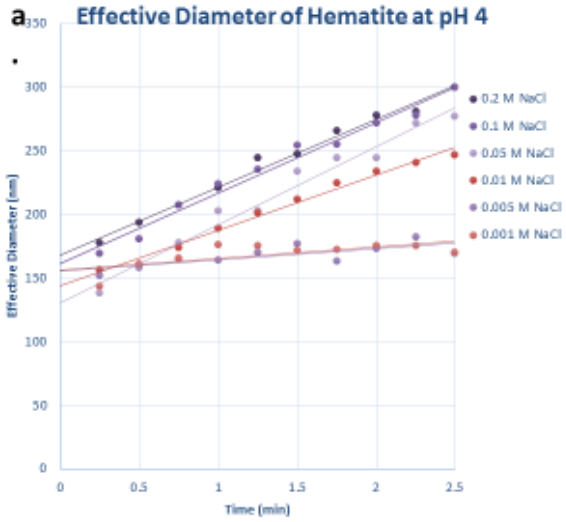

Figure A14. Aggregation results of hematite with 30 µM citric acid at pH 4.

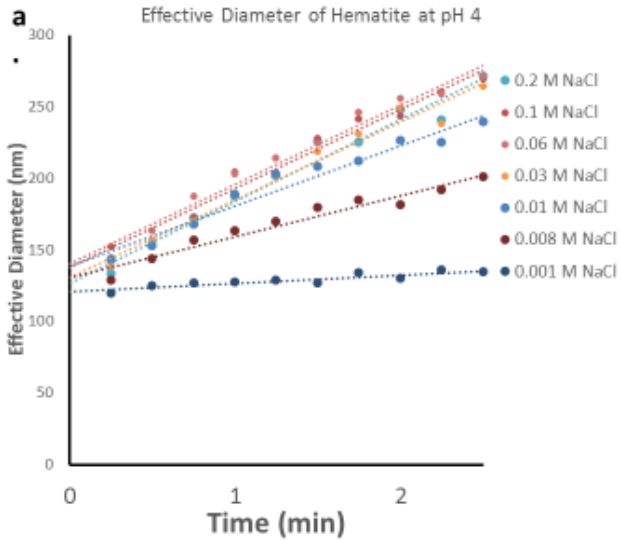

Figure A15. Aggregation results of hematite with 300 µM citric acid at pH 4.

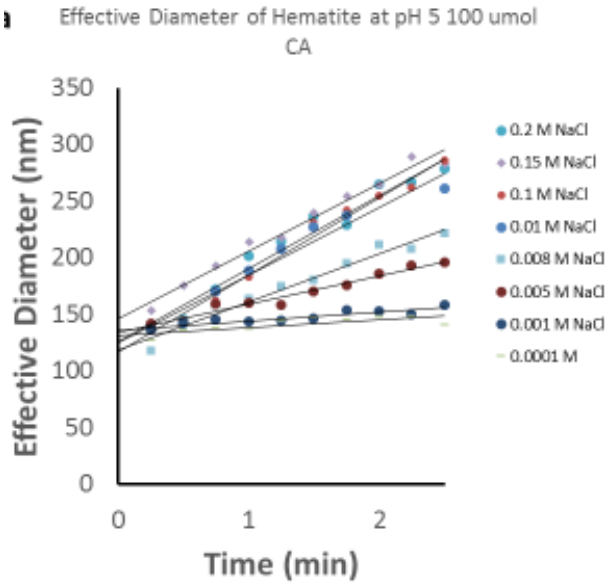

Figure A16. Aggregation results of hematite with 1.5 µM citric acid at pH 5.

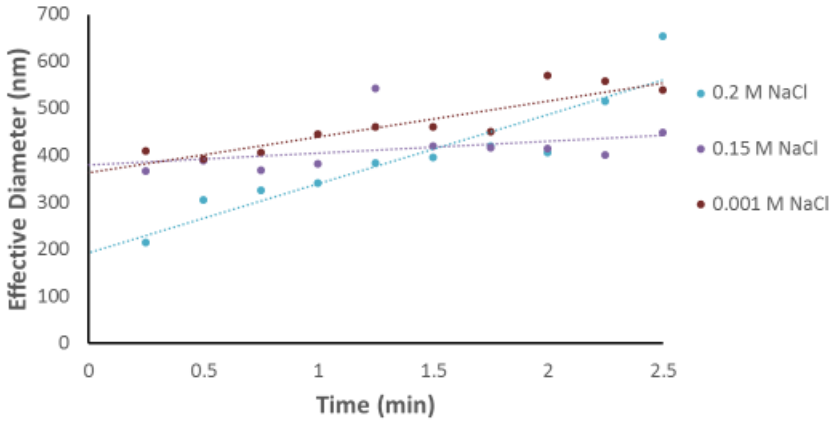

Figure A17. Aggregation results of hematite with 15 µM citric acid at pH 5.

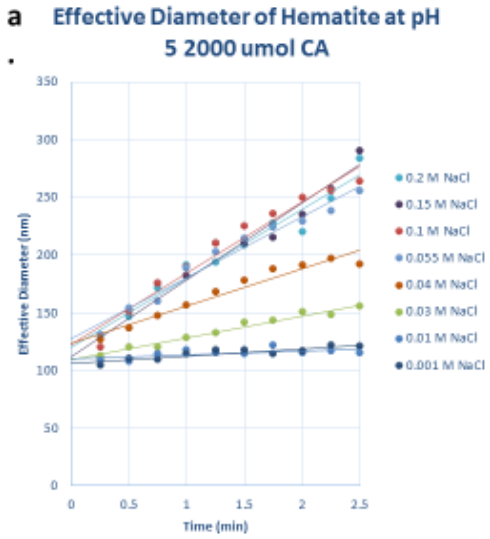

Figure A18. Aggregation results of hematite with 30 µM citric acid at pH 5.

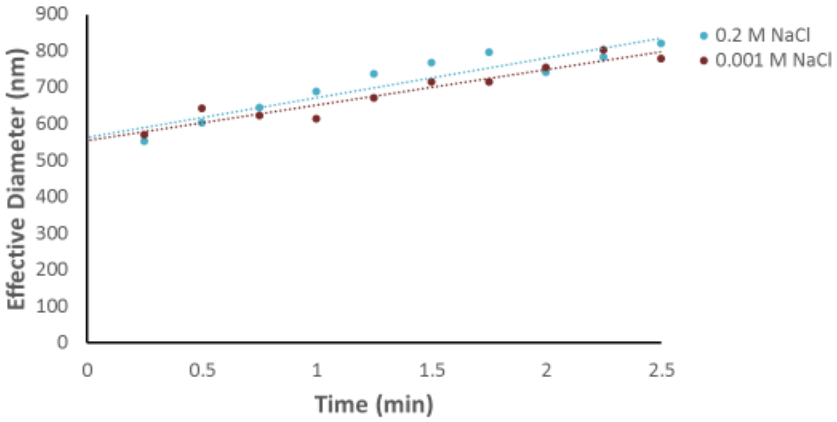

Figure A19. Aggregation results of hematite with 300 μM citric acid at pH 5.

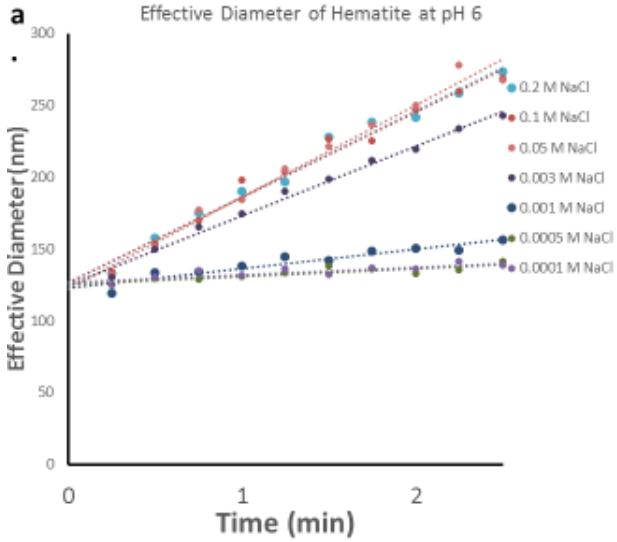

Figure A20. Aggregation results of hematite with 1.5 μM citric acid at pH 6.

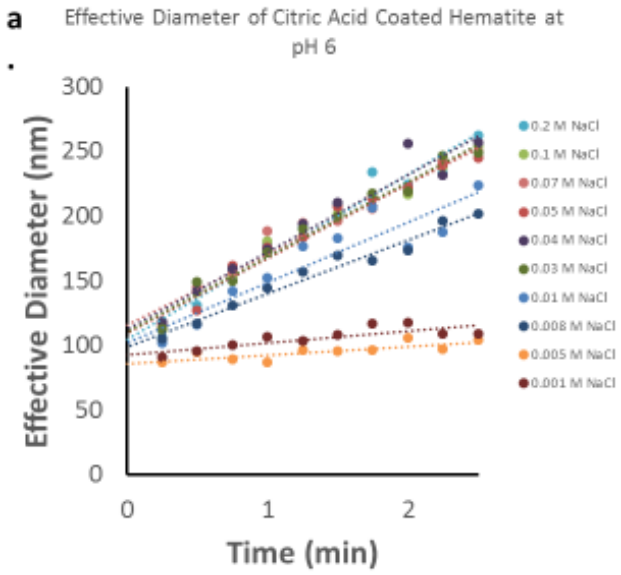

Figure A21. Aggregation results of hematite with 15 μM citric acid at pH 6.

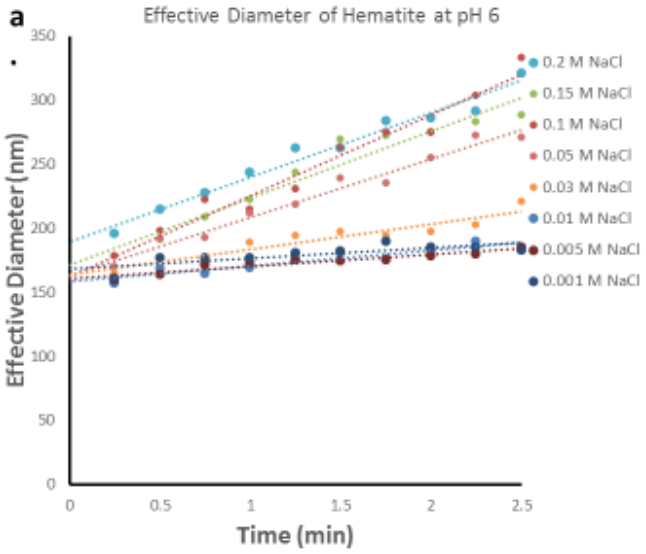

Figure A22. Aggregation results of hematite with 30 µM citric acid at pH 6.

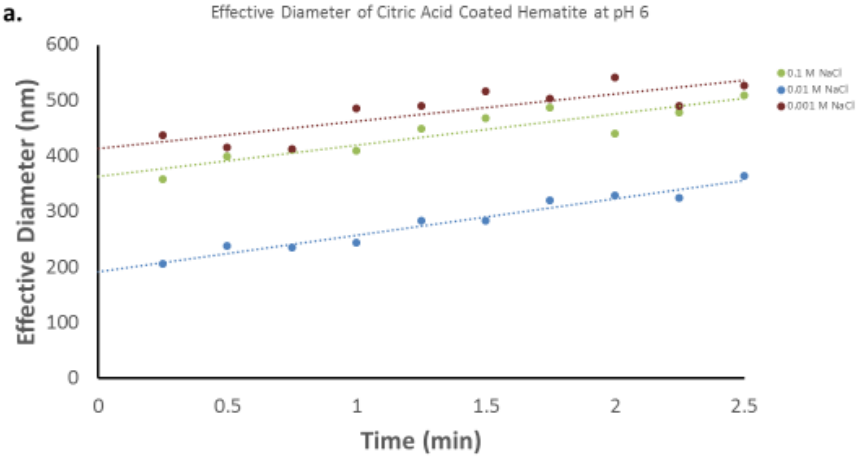

Figure A23. Aggregation results of hematite with 300 µM citric acid at pH 6.

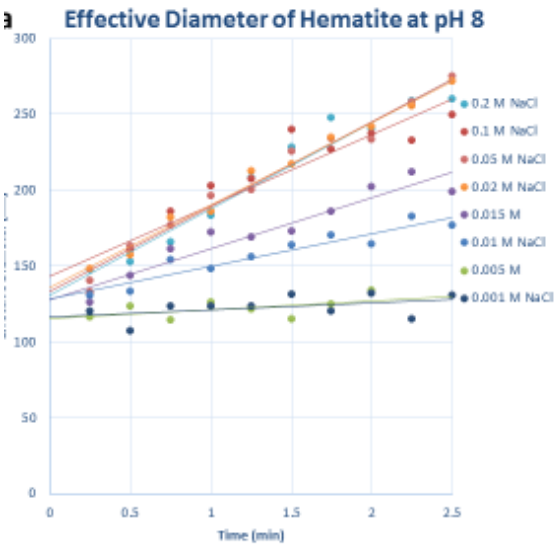

Figure A24. Aggregation results of hematite with 1.5 μM citric acid at pH 8.

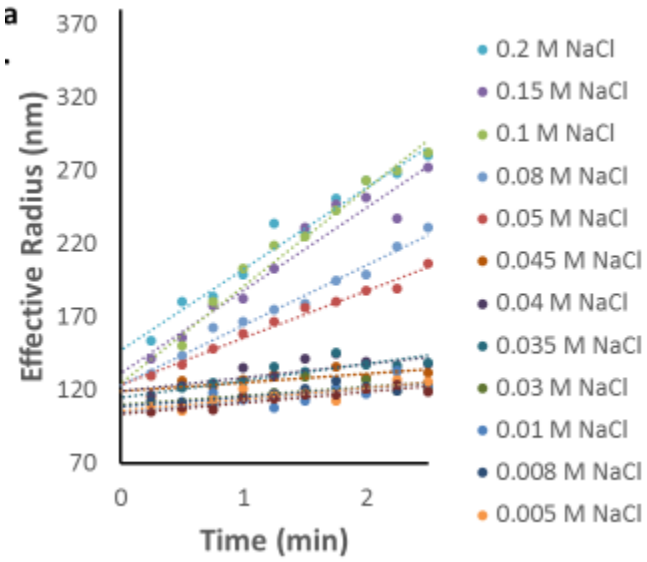

Figure A25. Aggregation results of hematite with 30 μM citric acid at pH 8.

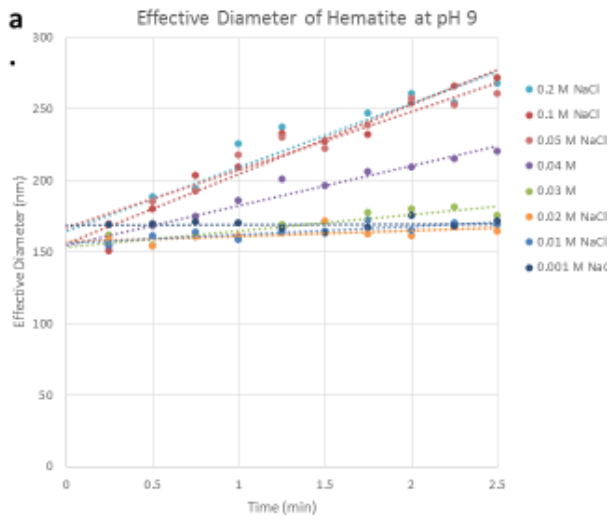

Figure A26. Aggregation results of hematite with 1.5 μM citric acid at pH 9.

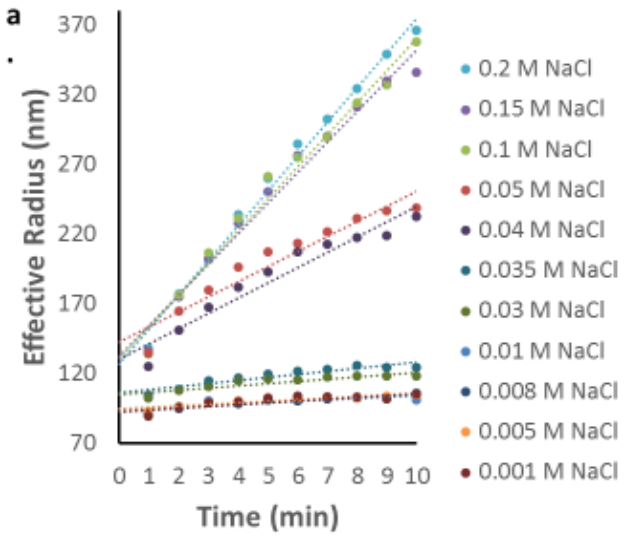

Figure A27. Aggregation results of hematite with 15 μM citric acid at pH 9.

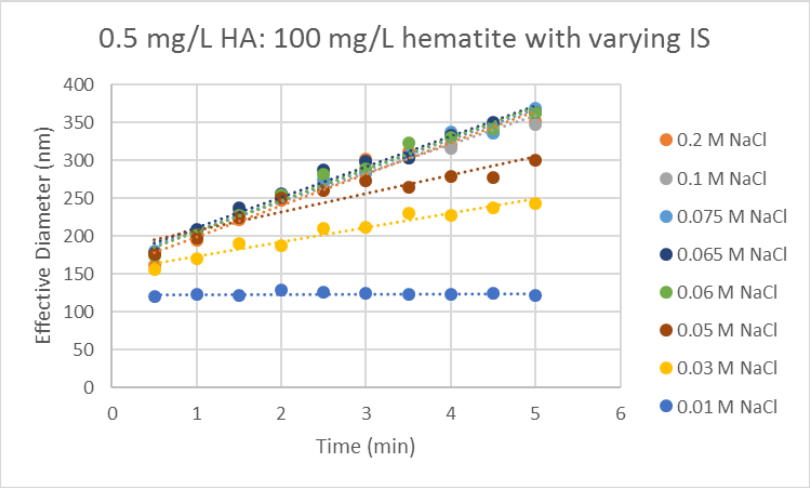

Figure A28. Effective diameter as a function of time for hematite with 2.2 μM humic acid at pH 6.